PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C11D 17/00, 1/37, 3/37, 3/42 // 1:22, 1:14

A1

(11) International Publication Number: **WO 00/05334**

(43) International Publication Date: 3 February 2000 (03.02.00)

(21) International Application Number: PCT/US98/15349

(22) International Filing Date: 23 July 1998 (23.07.98)

(71) Applicant *(for all designated States except US)*: THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: SHENA, Vinay, Madhav [IN/PH]; Unit 402, Orient Mansion Condo, Tordesellas St., Salcedo Village, Makati City 1227 (PH). GONZALES, Elma Quiaonza [PH/PH]; 21 San Rafael Sto. Thomas, 4234 Batangas (PH).

(74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: LAUNDRY DETERGENT COMPOSITION

(57) Abstract

The present invention is directed to a laundry detergent bar composition which includes an anionic surfactant system including a linear alkylbenzene sulfonate and an alkyl sulfate, and the combination of a certain modified polyethyleneimine polymer and a stilbenedisulfonate brightener to provide improved dye transfer inhibition.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav Republic of Macedonia	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece			**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's Republic of Korea	**NZ**	New Zealand		
CM	Cameroon			**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

LAUNDRY DETERGENT COMPOSITION

FIELD

The present invention relates to a laundry detergent composition. Specifically, the present invention relates to a laundry detergent composition containing a synthetic anionic surfactant.

BACKGROUND

In societies where mechanical washing machines are not common, laundry detergents comprising synthetic organic surfactants and detergency builders are used, for example, in the laundering of clothes. A common problem which arises when washing a fabric in a wash solution is the tendency of some colored fabrics to release dye, or a "fugitive dye," into the wash solution. The fugitive dye often transfers to other fabrics in the same wash solution and/or re-deposits onto the original fabric. The fugitive dye may discolor or otherwise stain the fabric, which is highly undesirable.

One approach in addressing this dye transfer problem has been to add "dye transfer inhibitors" (DTIs) to a laundry detergent composition. The DTIs are typically polymeric materials which complex or adsorb fugitive dyes in the wash solution, and thereby prevent the fugitive dye from transferring and/or re-depositing onto the fabric. Examples of such DTIs include, for example, polymers and copolymers of polyvinylpyrrolidone, carboxymethyl cellulose, vinylpyrrolidone, etc.

In many locales, such a laundry detergent composition takes the form of a laundry detergent bar. Technical developments in the field of laundry detergent bars have concerned formulating laundry detergent bars which are effective in cleaning clothes; which have acceptable sudsing characteristics in warm and cool water, and in hard and soft water; which have acceptable in-use wear rates, hardness, durability, and feel; which have low smear; and which have a pleasing odor and appearance. Laundry detergent bar processes are also well known in

the art. Prior art disclosing laundry detergent bars and laundry detergent bar processes include: U.S. Patent 3,178,370, Okenfuss, issued April 13, 1965; and Philippine Patent 13778 to Anderson, issued September 23, 1980.

Sudsing characteristics are also very important in the laundry detergent bar and hand-wash context. In contrast to the washing machine context, where high sudsing is undesirable, high sudsing characteristics are highly desirable when laundry detergent bars are used for hand-washing. In the hand-washing context, the amount of suds and the durability of the lather formed is directly observable. Because consumers directly correlate high sudsing characteristics with high cleaning ability, a laundry detergent bar which produces both a large volume of suds and long-lasting suds, is highly preferred by consumers. While a laundry detergent bar which has inherently inferior sudsing characteristics will often include a suds booster, high levels of such a suds booster raise the formulation costs of the bar.

Accordingly, the need remains for an improved laundry detergent, and especially a laundry detergent bar, which provides improved dye transfer inhibition benefits as well as high sudsing characteristics.

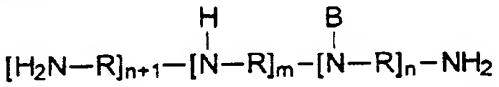
BACKGROUND ART

Patent Publication WO95/32272, published November 30, 1995, discloses the use of alkoxylated, especially ethoxylated and/or propoxylated polyalkyleneamine polymers as soil release agents in synthetic laundry detergent bar products. The following discloses various soil release polymers or modified polyamines: U.S. Patent 4,548,744, Connor, issued October 22, 1985; U.S. Patent 4,597,898, Vander Meer, issued July 1, 1986; U.S. Patent 4,877,896, Maldonado, et al., issued October 31, 1989; U.S. Patent 4,891,160, Vander Meer, issued January 2, 1990; U.S. Patent 4,976,879, Maldonado, et al., issued December 11, 1990; U.S. Patent 5,415,807, Gosselink, issued May 16,1995; U.K. Patent 1,537,288, published December 29, 1978; U.K. Patent 1,498,520, published January 18, 1978; German Patent DE 28 29 022, issued January 10, 1980; Japanese Kokai JP 06313271, published April 27, 1994.

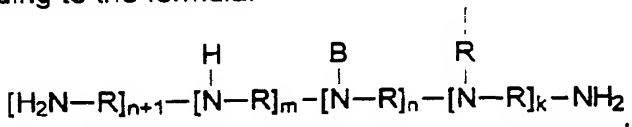
SUMMARY

It has now been found that a synergistic combination of certain ingredients in a laundry detergent composition addresses fugitive dye transfer problems in

wash solutions, while simultaneously providing desirable sudsing characteristics. The present invention is directed to laundry detergent compositions which contain, by weight of the final composition from about 5% to about 30% of an anionic surfactant system, which includes a linear alkylbenzene sulfonate and a coconut fatty alkyl sulfate. The laundry detergent bar also contains from about 0.05% to about 5% of a modified polyethyleneimine polymer with a polyamine backbone prior to modification via quaternization, substitution, or oxidation corresponding to the formula:

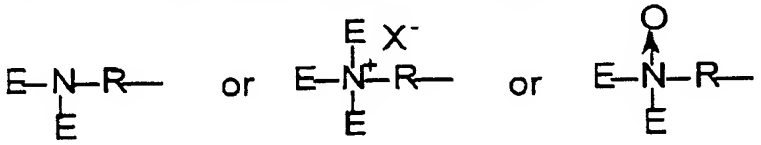


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone prior to modification via quaternization, substitution, or oxidation corresponding to the formula:



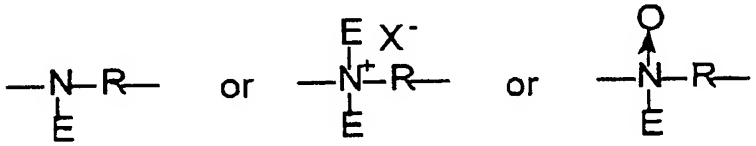
having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

i) V units are terminal units having the formula:



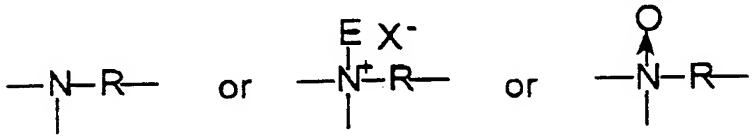
;

ii) W units are backbone units having the formula:



;

iii) Y units are branching units having the formula:



; and

iv) Z units are terminal units having the formula:

wherein backbone linking R units are selected from the group consisting of C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R^1 is C_2-C_6 alkylene and mixtures thereof; R^2 is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R^3 is C_1-C_{18} alkyl, C_7-C_{12} arylalkyl, C_7-C_{12} alkyl substituted aryl, C_6-C_{12} aryl, and mixtures thereof; R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, and mixtures thereof; R^5 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, -C(O)-, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof; R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene; E units are selected from the group consisting of hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is hydrogen, C_1-C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1.

The laundry detergent bar also contains from about 0.01% to about 5% of a stilbenedisulfonate brightener, and the balance adjunct ingredients.

DETAILED DESCRIPTION

In accordance with the present invention it has been found that in a laundry detergent composition having linear alkyl benzene sulfonate, coconut fatty alkyl sulfate, a certain modified polyethyleneimine polymer, and a stilbenedisulfonate brightener unexpectedly provides significantly improved dye transfer inhibition benefits. In addition to providing surprising dye transfer inhibition benefits across a wide range of dyes, the laundry detergent composition of the present invention also provide surprisingly high sudsing characteristics.

All percentages, ratios and proportions herein are by weight, unless otherwise specified. All temperatures are in degrees Celsius (°C) unless otherwise specified. All documents cited herein are incorporated by reference.

As used herein, the term "alkyl" means a hydrocarbyl moiety which is straight or branched, saturated or unsaturated. Unless otherwise specified, alkyl moieties are preferably saturated or unsaturated with double bonds, preferably with one or two double bonds.

The term "coconut oil" is used herein in connection with materials with fatty acid mixtures which typically are linear and have an approximate carbon chain length distribution of about 8% C_8, 7% C_{10}, 48% C_{12}, 17% C_{14}, 9% C_{16}, 2% C_{18}, 7% oleic, and 2% linoleic (the first six fatty acids listed being saturated). Other sources having a similar carbon chain length distribution in their fatty acids, such as palm kernel oil and babassu oil, are included within the term coconut oil.

The term "moisture" as used herein includes both free and bound moisture, as well as free and bound water.

The term "tallow" is used herein in connection with materials with fatty acid mixtures which typically are linear and have an approximate carbon chain length distribution of 2% C_{14}, 29% C_{16}, 23% C_{18}, 2% palmitoleic, 41% oleic, and 3% linoleic (the first three fatty acids listed are saturated). Other mixtures with similar distribution, such as those from palm oil and those derived from various animal tallow and lard, are also included within the term tallow. The

The laundry detergent composition of the current invention contains an anionic surfactant system including a linear alkylbenzene sulfonate and a coconut alkyl sulfate, a modified polyethyleneimine polymer, a stilbenedisulfonate brightener, and adjunct ingredients. The current invention provides a number of surprising benefits. For example, the laundry detergent composition of the present invention shows improved dye transfer inhibition benefits for a wide range of dye types, such as, for example, disperse dyes, chroma dyes, rota dyes, acid dyes, and other dye types. Furthermore, the laundry detergent composition described herein shows dye transfer inhibition benefits for a wide range of fabric types, such as, for example, cotton, polycotton, polyester, and polyrayon.

The laundry detergent composition of the current invention also provides high sudsing characteristics, which consumers correlate with high cleaning ability. The improved sudsing characteristics include a larger volume of suds, as well as longer lasting suds than, for example, a laundry detergent formulation containing soap and an anionic surfactant. This lowers formulation costs, as less suds booster need be added into the laundry detergent formulation.

Further benefits of the laundry detergent composition described herein include improved stain removal, cleaning and whitening benefits, which can potentially lower formulation costs by reducing the number of additional agents needed in laundry detergent formulations. Additionally, the benefits produced by the combination described herein also allow a reduction of the surfactant level in the laundry detergent formulation, further leading to lowered formulation costs.

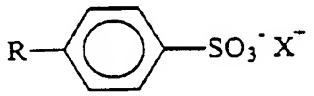
In a highly preferred embodiment of the invention, the laundry detergent composition described herein is in the form of a laundry detergent bar. The present invention provides distinct advantages in a laundry detergent bar because the direct application thereof to a fabric increases the effectiveness of the dye transfer inhibition benefits. Additionally, because laundry detergent bars are commonly used for hand washing in areas with water having a high hardness (i.e., greater than about 10 grains/gallon), the sudsing benefits (especially as compared to soap-containing laundry detergent bars) described herein are more readily observable in a laundry detergent bar/hand wash context.

Anionic Surfactant System

The laundry detergent composition of the current invention contains, by weight of the final composition, from about 5% to about 30%, preferably from

about 10% to about 25%, and more preferably from about 16% to about 25%, of an anionic surfactant system. The anionic surfactant system of the laundry detergent bar of the current invention contains both a linear alkylbenzene sulfonate (LAS), and a coconut fatty alkyl sulfate (CFAS). Other anionic surfactants may be contained herein as well.

The LAS useful herein has the general formula:



;

wherein, R represents an alkyl group of from about 10 to about 20 carbon atoms, and X^+ represents a cationic species, preferably an alkali metal salt or ammonium moiety. Of the alkali metal salts, the sodium and potassium salts of these surfactants are particularly preferred.

The LAS suitable for use herein includes the water-soluble salts, preferably the alkali metal, ammonium and alkylolammonium salts of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. LAS and other carbon chain based compounds herein are abbreviated according to the average alkyl group length. For example, LAS with an average chain length of 12 carbon atoms is abbreviated as C_{12} LAS, even though it contains a distribution of LAS molecules with alkyl groups of differing lengths. The LAS raw material useful herein is typically at least 90% LAS, preferably at least 95% LAS, with the remainder comprising a combination of linear alkyl benzene, moisture, and/or sulfuric acid.

Processes for synthesizing the LAS useful herein are well known in the art. The typical process involves the sulfonation of a linear alkyl benzene, to form the linear alkyl benzene sulfonic acid. This acid is then neutralized with, for example, an alkaline sodium salt to form the corresponding sodium linear alkyl benzene sulfonate.

Unsulfonated linear alkyl benzene is available from, for example, P. T. Unggul Indah Corp. (Indonesia), Chemphil Group - LMG Chemicals Corp. (Batangas, Philippines), Isu Chemical Co., Ltd. (Korea), and Formosan Union Chemical Corp. (Taiwan). Alternatively, LAS is commercially available from, for example, Formosan Union Chemical Corp. and Isu Chemical Co., Ltd.

Especially valuable herein are linear chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to

13, abbreviated as C_{11-13} LAS. The amount of LAS suitable for use in the laundry detergent bar is from about 1% to about 30%, preferably from about 2% to about 20%, and more preferably from about 3% to about 15%, by weight of the final composition.

The CFAS suitable for use herein corresponds to the general formula:

$R\text{-}O\text{-}SO_3^- X^+$;

wherein, R represents an alkyl group of from about 8 to about 18 carbon atoms, and X^+ represents a cationic species, preferably an alkali metal salt. The CFAS suitable for use herein includes those used in detergent applications, particularly the sodium and potassium CFAS salts. These may be obtained by sulfating the higher alcohols (C_{8-18} carbon atoms) produced by reducing the glycerides of coconut oil.

The CFAS suitable for use herein is commercially available, for example, from Optimus Industrial Development, Inc. (Laguna, Philippines), Colgate (Quezon, Philippines), Lever (Philippines), Chemphil Group - LMG Chemicals Corp. (Batangas, Philippines), United Coconut Chemicals, Inc. (Batangas, Philippines), Pilipinas Kao, Inc. (Philippines), and Stepan Philippines, Inc. (Batangas, Philippines). Typically, CFAS is available as either a flake (dried to about 10% to about 20% moisture) and/or as a paste (typically about 20% to about 30% moisture). Both physical forms are useful herein, with a mixture thereof being preferred. The actual weight ratio of flake CFAS to paste CFAS depends primarily upon the desired moisture content of the final laundry detergent form. For example, if free water and moisture are to be minimized, then a flake may be preferable. In a laundry detergent bar, the typical weight ratio of CFAS flake to CFAS paste is from about 100:0 to about 30:70.

Preferred CFAS is C_{8-18} CFAS, especially C_{12} CFAS. CFAS is present in a laundry detergent bar at from about 1% to about 30%, preferably from about 4% to about 22%, more preferably from about 10% to about 18%, by weight of the final composition. In a preferred embodiment, the ratio of LAS to CFAS in the anionic surfactant system is from about 19:1 to 1:9, preferably from about 10:1 to about 1:5, and more preferably from about 4:1 to about 1:3, by weight, in the final composition.

Typically, the anionic surfactant system will further comprise a tallow alkyl sulfate. In such cases, the anionic surfactant system contains therein a mixture of fatty acids of tallow and coconut oil having a weight ratio of tallow:coconut

fatty acid of from about 85:15 to about 50:50, preferably from about 80:20 to about 65:35.

Other anionic surfactants are optionally included in the anionic surfactant system herein. For example, branched chain alkyl benzene sulfonates, branched-chain and random C_{10}-C_{20} alkyl sulfates ("AS"), the C_{10}-C_{18} secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3^-M^+)$ CH_3 and CH_3 $(CH_2)_y(CHOSO_3^-M^+)$ CH_2CH_3 where x and (y + 1) are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C_{10}-C_{18} alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), and mixtures thereof. The anionic surfactants useful herein may be provided in either as a pre-neutralized anionic surfactant and/or in the acid form, and neutralized herein.

It is preferred that the laundry detergent composition of the current invention be substantially free of soap (i.e., less than about 1% by weight of the final laundry detergent bar). Without intending to be limited by theory, it is believed that the addition of soap to the current invention leads to reduced sudsing characteristics, especially in hard water conditions (i.e., greater than about 10 grains/gallon).

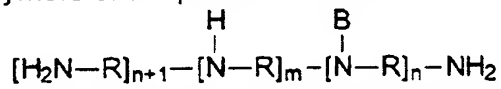
Modified Polyethyleneimine Polymer

The modified polyethyleneimine polymer of the present invention is a water-soluble or dispersible, modified polyamine. The amount of modified polyethyleneimine polymer suitable for use in the composition herein is from about 0.05% to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.3% to about 1.5%, by weight of the final composition. These modified polyethyleneimine polymers comprise backbones that may be either linear or cyclic. The polyamine backbones may also comprise polyamine branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

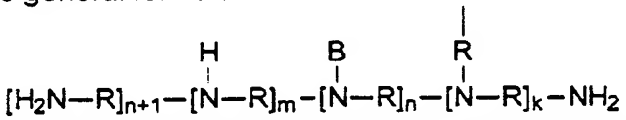
For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used

interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution is preferably accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the modified polyethyleneimine polymers of the present invention have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units. The cyclic polyamine backbones comprising the modified polyethyleneimine polymers of the present invention have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure:

$H_2N\text{-}R]\text{-}$

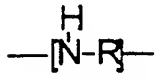
is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure:

$\text{-}NH_2$

is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

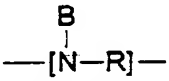
In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For

example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure:



is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, wherein B represents a continuation of the chain structure by branching, having the structure:



is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all or the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

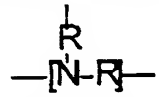
The final modified structure of the modified polyethyleneimine polymers of the present invention can be therefore represented by the general formula:

$$V_{(n+1)}W_mY_nZ$$

for linear modified polyethyleneimine polymers and by the general formula:

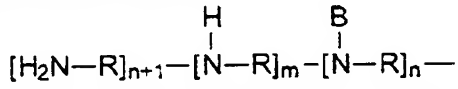
$$V_{(n-k+1)}W_mY_nY'_kZ$$

for cyclic modified polyethyleneimine polymers . For the case of modified polyethyleneimine polymers comprising rings, a Y' unit of the formula:



serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula:

that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula:



therefore comprising no Z terminal unit and having the formula:

$$V_{n-k}W_mY_nY'_k$$

wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic modified polyethyleneimine polymers, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyethyleneimine polymer according to the present invention has the formula:

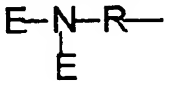
$$VW_mZ$$

that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to about 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

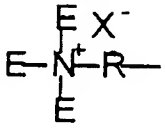
Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

Modified primary amine moieties are defined as V "terminal" units having one of three forms:

a) simple substituted units having the structure:

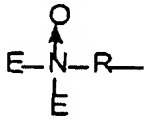


b) quaternized units having the structure:



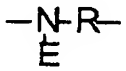
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

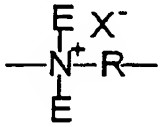


Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

a) simple substituted units having the structure:

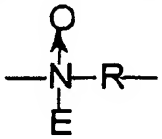


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

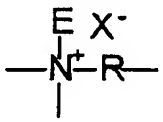
c) oxidized units having the structure:



Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

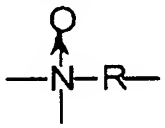
a) unmodified units having the structure:

b) quaternized units having the structure:



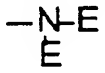
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

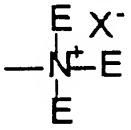


Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

a) simple substituted units having the structure:

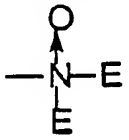


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

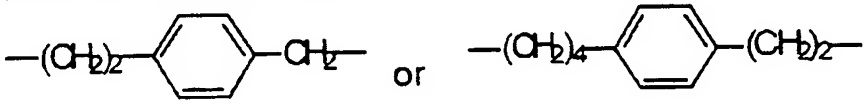


When any position on a nitrogen is unsubstituted of unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit comprising one E unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula:

$(HOCH_2CH_2)HN$-.

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure $-NH_2$. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore E cannot be a hydrogen.

The modified polyethyleneimine polymers of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_3-C_{12} hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C_4-C_{12} dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C_8-C_{12} dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula:



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C_2-C_{12} alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise -$(R^1O)_xR^5(OR^1)_x$-, -$CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w$-, -$CH_2CH(OR^2)CH_2$-, -$(R^1O)_xR^1$-, and mixtures thereof. Preferred R units are C_2-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, -$(R^1O)_xR^1$-, -$CH_2CH(OR^2)CH_2$-, -$(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH$-$(OH)CH_2)_w$-, -$(R^1O)_xR^5(OR^1)_x$-, more preferred R units are C_2-C_{12} alkylene, C_3-C_{12} hydroxy-alkylene, C_4-C_{12} dihydroxyalkylene, -$(R^1O)_xR^1$-, -$(R^1O)_xR^5(OR^1)_x$-, -$(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1(OCH_2CH$-$(OH)CH_2)_w$-, and mixtures thereof, even more preferred R units are C_2-C_{12} alkylene, C_3 hydroxyalkylene, and mixtures thereof, most preferred are C_2-C_6 alkylene. The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

R^1 units are C_2-C_6 alkylene, and mixtures thereof, preferably ethylene. R^2 is hydrogen, and -$(R^1O)_xB$, preferably hydrogen.

R^3 is C_1-C_{18} alkyl, C_7-C_{12} arylalkylene, C_7-C_{12} alkyl substituted aryl, C_6-C_{12} aryl, and mixtures thereof , preferably C_1-C_{12} alkyl, C_7-C_{12}

arylalkylene, more preferably C_1-C_{12} alkyl, most preferably methyl. R^3 units serve as part of E units described herein below.

R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, preferably C_1-C_{10} alkylene, C_8-C_{12} arylalkylene, more preferably C_2-C_8 alkylene, most preferably ethylene or butylene.

R^5 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxyalkylene, C_8-C_{12} dialkylarylene, -C(O)-, -C(O)NHR^{6}NHC(O)-, -C(O)(R^4)$_r$C(O)-, -R^1(OR^1)-, -$CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2$-, -C(O)($R^4$)$_r$C(O)-, -$CH_2CH(OH)CH_2$-, R^5 is preferably ethylene, -C(O)-, -C(O)NHR^{6}NHC(O)-, -R^1(OR^1)-, -$CH_2CH(OH)CH_2$-, -$CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH$-(OH)$CH_2$-, more preferably -$CH_2CH(OH)CH_2$-.

R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene.

The preferred "oxy" R units are further defined in terms of the R^1, R^2, and R^5 units. Preferred "oxy" R units comprise the preferred R^1, R^2, and R^5 units. The preferred modified polyethyleneimine polymers of the present invention comprise at least 50% R^1 units that are ethylene. Preferred R^1, R^2, and R^5 units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

i) Substituting more preferred R^5 into -$(CH_2CH_2O)_xR^5(OCH_2CH_2)_x$- yields -$(CH_2CH_2O)_xCH_2CHOHCH_2(OCH_2CH_2)_x$-.

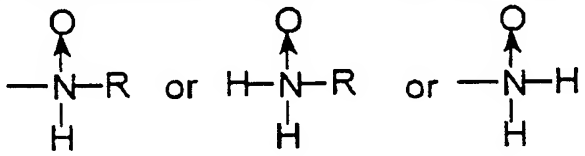
ii) Substituting preferred R^1 and R^2 into -$(CH_2CH(OR^2)CH_2O)_z$-$(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w$- yields -$(CH_2CH(OH)CH_2O)_z$-$(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w$-.

iii) Substituting preferred R^2 into -$CH_2CH(OR^2)CH_2$- yields -$CH_2CH(OH)CH_2$-.

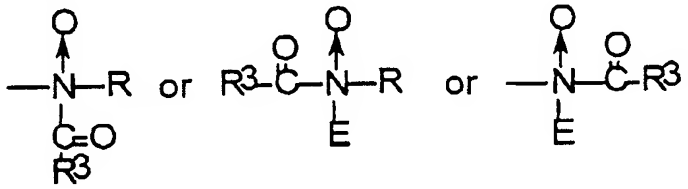
E units are selected from the group consisting of hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxyalkyl, -$(CH_2)_pCO_2M$, -$(CH_2)_qSO_3M$, -$CH(CH_2CO_2M)CO_2M$, -$(CH_2)_pPO_3M$, -$(R^1O)_mB$, -C(O)R^3, preferably hydrogen, C_2-C_{22} hydroxyalkylene, benzyl, C_1-C_{22} alkylene, -$(R^1O)_mB$, -C(O)R^3, -$(CH_2)_pCO_2M$, -$(CH_2)_qSO_3M$, -$CH(CH_2CO_2M)CO_2M$, more

preferably C_1-C_{22} alkylene, -$(R^1O)_xB$, -$C(O)R^3$, -$(CH_2)_pCO_2M$, -$(CH_2)_qSO_3M$, -$CH(CH_2CO_2M)CO_2M$, most preferably C_1-C_{22} alkylene, -$(R^1O)_xB$, and -$C(O)R^3$. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

E units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



Additionally, E units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the E unit -$C(O)R^3$ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure:



or combinations thereof.

B is hydrogen, C_1-C_6 alkyl, -$(CH_2)_qSO_3M$, -$(CH_2)_pCO_2M$, -$(CH_2)_q$-$(CHSO_3M)CH_2SO_3M$, -$(CH_2)_q(CHSO_2M)CH_2SO_3M$, -$(CH_2)_pPO_3M$, -$PO_3M$, preferably hydrogen, -$(CH_2)_qSO_3M$, -$(CH_2)_q(CHSO_3M)CH_2SO_3M$, -$(CH_2)_q$-$(CHSO_2M)CH_2SO_3M$, more preferably hydrogen or -$(CH_2)_qSO_3M$.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies -$(CH_2)_pCO_2M$, and -$(CH_2)_qSO_3M$, thereby resulting in -$(CH_2)_pCO_2Na$, and -$(CH_2)_qSO_3Na$ moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one monovalent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a -$(CH_2)_pPO_3M$ moiety substituted with sodium atoms has the formula -$(CH_2)_pPO_3Na_3$. Divalent

cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable monovalent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine (I^-) or X can be any negatively charged radical such as sulfate (SO_4^{2-}) and methosulfate ($CH_3SO_3^-$).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; m has the value from 4 to about 400, n has the value from 0 to about 200; m + n has the value of at least 5.

The preferred modified polyethyleneimine polymers of the present invention comprise polyamine backbones wherein less than about 50% of the R groups comprise "oxy" R units, preferably less than about 20% , more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

The most preferred modified polyethyleneimine polymers which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C_2-C_{12} alkylene, preferred is C_2-C_3 alkylene, most preferred is ethylene.

The modified polyethyleneimine polymers of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a

homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone. The proper manipulation of these "R unit chain lengths" provides the formulator with the ability to modify the solubility and fabric substantivity of the modified polyethyleneimine polymers of the present invention.

Preferred modified polyethyleneimine polymers of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylenepentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and teraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C_2 alkylene (ethylene) units, also known as polyethyleneimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:

$$[H_2N-CH_2CH_2]_{n+1}-[N(H)-CH_2CH_2]_m-[N(B)-CH_2CH_2]_n-NH_2$$

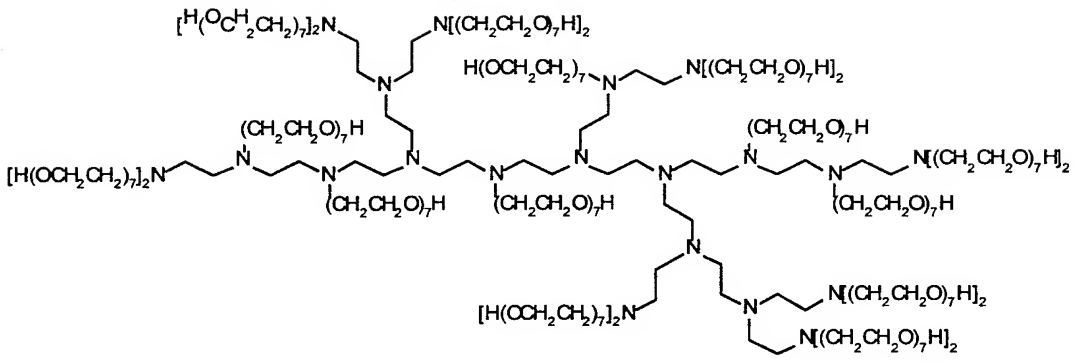
wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These modified polyethyleneimine polymers can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

Examples of modified polyethyleneimine polymers of the present invention comprising PEI's, are illustrated in Formulas I - IV:

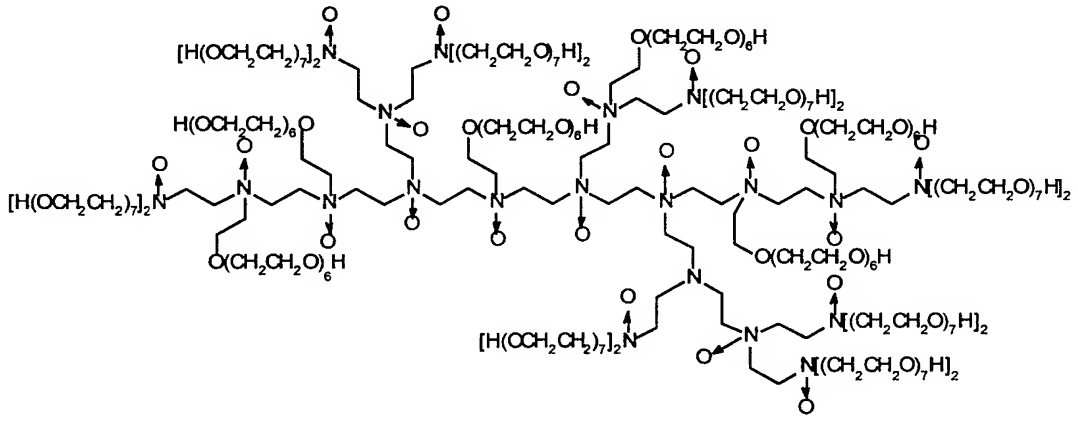
Formula I depicts a modified polyethyleneimine polymer comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, having the formula:



Formula I

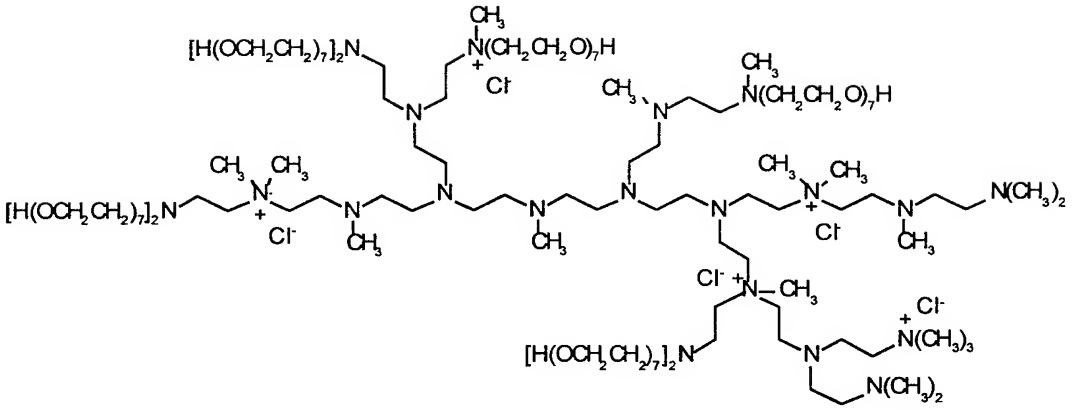
This is an example of a modified polyethyleneimine polymer that is fully modified by one type of moiety.

Formula II depicts a modified polyethyleneimine polymer comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_7H$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, said modified polyethyleneimine polymer having the formula:



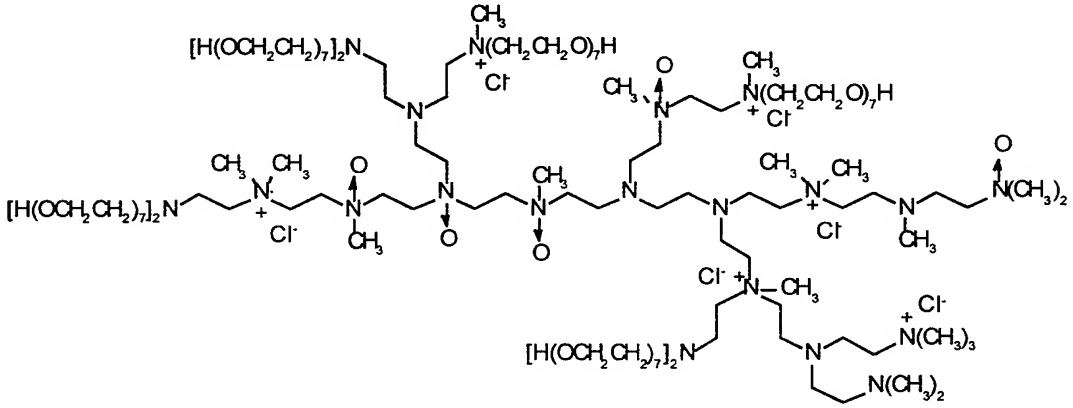
Formula II

Formula III depicts a modified polyethyleneimine polymer comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(CH_2CH_2O)_7H$, or methyl groups. The modified PEI soil release polymer has the formula:



Formula III

Formula IV depicts a modified polyethyleneimine polymer comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(CH_2CH_2O)_7H$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting modified polyethyleneimine polymer has the formula:



Formula IV

In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

Stilbenedisulfonate Brightener

A stilbenedisulfonate brightener is included in the laundry detergent composition of the present invention. The stilbenedisulfonate brighteners are known in laundry detergent compositions as a class of florescent whitening agents and/or as optical brighteners. Such florescent whitening agents, when deposited onto a fabric, convert ultraviolet light into visible wavelength light, thus making the fabric appear brighter and more vivid to the human eye. Without intending to be limited by theory, it is believed that in addition to these brightener effects, a stilbenedisulfonate brightener and a modified polyethyleneimine polymer interact with the surfactant system to provide enhanced dye transfer inhibition effects. A preferred stilbenedisulfonate brightener is a derivative of diamino stilbene.

A nonlimiting example of a stilbenedisulfonate brightener useful herein includes 4,4'-bis{[4-anilino-6-bis(2-hydoxyethyl) amino-1,3,5-trizin-2-yl]amino}stilbene-2,2'-disulfonic acid disodium salt, 4,4'-bis[(4-anilino-6-morpholino-1,3,5-triazin-2-yl) amino]stilbene-2,2'-disulfonic acid disodium salt, the 4,4'-bis- (1,2,3-triazol-2-yl)-stilbenes, 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole, and mixtures thereof. These are available, for example, as Brightener 3, Brightener 15, Brightener 24, Brightener 36, Brightener 47, Brightener 64, and Brightener 70, from Ciba Specialty Chemicals (Greenboro, USA; Monthey, Switzerland), Bayer Corp. (South Carolina, USA), Hilton-Davis (Italy), and 3V Inc. (Georgetown, USA). Examples of a stilbenedisulfonate brightener useful in the present composition are identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. Mixtures of stilbenedisulfonate brighteners are preferred herein.

The total stilbenedisulfonate brightener level in the laundry detergent bar may be from about 0.01% to about 5%, preferably from about 0.05% to about 1.2%, and more preferably from about 0.05% to about 0.5%, by weight of the final laundry detergent.

Adjunct Ingredients

The balance of the laundry detergent composition disclosed herein contains adjunct ingredients, some non-limiting examples of which are listed

below. Unless otherwise noted, all of the percentages below are by weight of the final composition.

If in the form of a solid composition, including a laundry detergent bar, the compositions of the subject invention comprise from about 0.5% to about 30% moisture, preferably from about 1% to about 10% moisture, more preferably from about 2% to about 6% moisture. For other laundry detergent forms, for example, liquid detergent compositions, the moisture level may be significantly higher.

Examples of a builder useful herein are the phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof. The water soluble alkali metal salts of these builders are preferred. A preferred builder is a phosphate builder such as the water soluble alkali metal salts of tripolyphosphates, and a mixture of tripolyphosphates and pyrophosphates. Specific preferred examples of a builder useful herein include the sodium tripolyphosphates (STPP), tetra sodium pyrophosphates (TSPP), and mixtures thereof.

The level of builder can vary widely depending upon the end use of the laundry detergent composition and its desired physical form. When present, the laundry detergent composition will typically comprise at least about 1% builder. Liquid detergent formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular detergent formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder. The laundry detergent bar of the present invention contains from about 3% to about 60%, preferably from about 5% to about 50%, more preferably from about 10% to about 30% builder, by weight of the final composition.

The laundry detergent composition of the present invention may optionally contain in addition to phosphate builders, non-phosphate builders. Specific examples of a non-phosphate builder, such as inorganic detergency builders, include the water soluble inorganic carbonate and bicarbonate salts. The alkali metal (e.g., sodium and potassium) carbonates and bicarbonates are particularly useful herein. Other specifically preferred examples of a builder useful herein include polycarboxylates.

Co-polymers of acrylic acid and maleic acid are preferred in the subject compositions as auxiliary builders, since it has been observed that their use in

combination with fabric softening clay and clay flocculating agents further stabilizes and improves the clay deposition and fabric softening performance.

In addition to the DTI benefits provided by the present invention, a preferred adjunct ingredient in the laundry detergent composition is an other dye transfer inhibitor ("other DTI") ingredient to further prevent diminishing of color fidelity and intensity in fabrics, and the transfer of dyes. These other DTI ingredients may complement and further enhance the dye transfer inhibition benefits of the present invention. A preferred other DTI ingredient includes a traditional polymeric dye transfer inhibition material capable of binding fugitive dyes to prevent them from depositing on the fabrics, a decolorization dye transfer inhibition material capable of decolorizing the fugitives dye by oxidation, or a combination thereof. Non-limiting, preferred examples of an other DTI ingredient includes polyvinylpyrridine N-oxide (PVNO), polyvinylpyrrolidone (PVP), polyvinylimidazole, N-vinylpyrrolidone and N-vinylimidazole copolymers (referred to as "PVPI"), copolymers thereof, and mixtures thereof. An example of an other DTI ingredient which provides dye transfer inhibition effects via decolorization is hydrogen peroxide or a hydrogen peroxide source, such as percarbonate or perborate.

The amount of other DTI ingredient included in the subject compositions, if any, is less than about 5%, preferably from about 0.05% to about 3%, more preferably from about 0.1% to about 2%, by weight of the final composition.

In addition to a stilbenedisulfonate brightener, other classes of florescent whitening agent, herein described as an "other brightener" may be included as an adjunct ingredient in the laundry detergent of the present invention. An especially preferred other brightener useful herein includes, for example, disodium 4,4'-bis-(2 sulfostyryl)biphenyl, also known as Brightener-49, analogs thereof, and combinations thereof. Such an other brightener is available from, for example, Ciba Giegy, under the tradename TINOPAL CBS.

Soil suspending agents can also be used herein. In the present invention, their use is balanced with the fabric softening clay/clay flocculating agent combination to provide optimum cleaning and fabric softening performance. One such soil suspending agent is an acrylic/maleic copolymer, commercially available as Sokolan®, from BASF Corp. Other soil suspending agents include polyethylene glycols having a molecular weight of about 400 to 10,000, and ethoxylated mono- and polyamines, and quaternary salts thereof. A highly preferred soil suspending agent is a water-soluble salt of carboxymethylcellulose

and carboxyhydroxymethylcellulose. Soil suspending agents may be used at levels up to about 5%, preferably about 0.1% to about 1%, by weight of the laundry detergent bar

The laundry detergent composition of the present invention may contain an optional surfactant commonly used in detergent products, such as a cationic surfactant, a nonionic surfactant, an amphoteric surfactant, a zwitterionic surfactant, and mixtures thereof. A typical listing of the classes and species of optional surfactants, optional alkaline builders such as sodium carbonate trisodium phosphate sodium silicate, etc. and other ingredients useful herein appears in U.S. Pat. No. 3,664,961, issued to Norris on May 23, 1972, and EP 550,652, published on April 16, 1992. Such optional surfactants, if present, can be included at levels up to a total of about 10%, preferably from about 0.5% to about 5%, by weight, of the laundry detergent bar. It is preferred that a nonionic surfactant be included herein.

The laundry detergent composition may optionally contain a fabric softening clay, preferably a smectite-type clay. The smectite-type clays can be described as expandable, three-layer clays; i.e., alumino-silicates and magnesium silicates, having an ion exchange capacity of at least about 50 meq/100 g. of clay. Preferably the clay particles are of a size that they can not be perceived tactilely, so as not to have a gritty feel on the treated fabric of the clothes. The fabric softening clay can be added to provide about 1% to about 50%, preferably from about 2% to about 20%, and more preferably about 3% to 14% by weight of the final composition.

While any of the smectite-type clays described herein are useful in the present invention, certain clays are preferred. For example, Gelwhite GP is an extremely white form of smectite-type clay and is therefore preferred when formulating white granular detergent compositions. Volclay BC, which is a smectite-type clay mineral containing at least 3% iron (expressed as Fe_2O_3) in the crystal lattice, and which has a very high ion exchange capacity, is one of the most efficient and effective clays for use in the instant compositions from the standpoint of product performance. On the other hand, certain smectite-type clays are sufficiently contaminated by other silicate minerals that their ion exchange capacities fall below the requisite range; such clays are of no use in the instant compositions.

Another preferred optional component in the laundry detergent composition is a secondary fabric softener component in addition to the

softening clay. Such materials may be used, if any, at levels of about 0.1% to 5%, more preferably from 0.3% to 3%, and include: amines of the formula $R_4R_5R_6N$, wherein R_4 is C_5 to C_{22} hydrocarbyl, R_5 and R_6 are independently C_1 to C_{10} hydrocarbyl. One preferred amine is ditallowmethyl amine; complexes of such amines with fatty acid of the formula R_7COOH, wherein R_7 is C_9 to C_{22} hydrocarbyl, as disclosed in EP No. 0,133,804; complexes of such amines with phosphate esters of the formula R_8O-P(O)(OH)-OR_9 and HO-P(O)(OH)-OR_9, wherein R_8 and R_9 are independently C_1 to C_{20} alkyl of alkyl ethoxylate of the formula -alkyl-(OCH_2CH_2); cyclic amines such as imidazolines of the general formula 1-(higher alkyl) amido (lower alkyl)-2-(higher alkyl)imidazoline, where higher alkyl is from 12 to 22 carbons and lower alkyl is from 1 to 4 carbons, such as described in UK Patent Application GB 2,173,827; and quaternary ammonium compounds of the formula $R_{10}R_{11}R_{12}R_{13}N^+X^-$, wherein R_{10} is alkyl having 8 to 20 carbons, R_{11} is alkyl having 1 to 10 carbons, R_{12} and R_{13} are alkyl having 1 to 4 carbons, preferably methyl, and X is an anion, preferably Cl^- or Br^-, such as C_{12-13} alkyl trimethyl ammonium chloride.

It has been found that the use of a clay flocculating agent in a laundry detergent composition containing a softening clay provides surprisingly improved softening clay deposition onto the clothes and clothes softening performance, compared to that a formula comprising softening clay alone. The polymeric clay flocculating agent provides improved deposition of the fabric softening clay, and typically, have a molecular weight greater than about 100,000. Examples of such materials include long chain polymers and copolymers derived from monomers such as ethylene oxide, acrylamide, acrylic acid, dimethylamino ethyl methacrylate, vinyl alcohol, vinyl pyrrolidone, and ethylene imine. Gums, like guar gums, are suitable as well. The preferred clay flocculating agent is a poly(ethylene oxide) polymer. The amount of clay flocculating agent, if any, is about 0.2-2%, preferably about 0.5-1%.

A particularly preferred adjunct ingredient herein is a detergent chelant. Such chelants sequester and chelate alkali cations (such as sodium, lithium and potassium), alkali metal earth cations (such as magnesium and calcium), and most importantly, heavy metal cations such as iron, manganese, zinc and aluminum. Preferred cations include sodium, magnesium, zinc, and mixtures thereof. The detergent chelant is particularly beneficial for maintaining good cleaning performance and improved surfactant mileage, despite the presence of

the softening clay and the clay flocculating agent. This is especially preferred in the laundry detergent bars of the current invention.

The detergent chelant is preferably a phosphonate chelant, particularly one selected from the group consisting of diethylenetriamine penta(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), and mixtures and salts and complexes thereof, and an acetate chelant, particularly one selected from the group consisting of diethylenetriamine penta(acetic acid), ethylene diamine tetra(acetic acid), and mixtures and salts and complexes thereof. Particularly preferred are sodium, zinc, magnesium, and aluminum salts and complexes of diethylenetriamine penta(methylene phosphonate) diethylenetriamine penta (acetate), and mixtures thereof.

Preferably such salts or complexes have a molar ratio of metal ion to chelant molecule of at least 1:1, preferably at least 2:1.

The detergent chelant may be included herein at a level up to about 5%, preferably from about 0.1% to about 3%, more preferably from about 0.2% to about 2%, even more preferably from about 0.5% to about 1.0%.

Another preferred additional component of the laundry detergent composition is fatty alcohol having an alkyl chain of 8 to 22 carbon atoms, more preferably from 12 to 18 carbon atoms. A preferred fatty alcohol has an alkyl chain predominantly containing from about 12 carbon atoms. Typically fatty alcohol, if any, is present in the laundry detergent composition at up to a level of 10%, more preferably from about 0.75% to about 6%, most preferably from about 2% to about 5%. The fatty alcohol is generally added to a laundry detergent composition as free fatty alcohol. However, low levels of fatty alcohol may be introduced into the bars as impurities or as unreacted starting material. For example, laundry detergent compositions based on coconut fatty alkyl sulfate can contain, as unreacted starting material, from 0.1% to 3.5%, more typically from 2% to 3%, by weight of free coconut fatty alcohol on a coconut fatty alkyl sulfate basis.

A highly preferred adjunct ingredient herein is a bleach component. The bleaching component may be a source of ^-OOH group, such as sodium perborate monohydrate, sodium perborate tetrahydrate and sodium percarbonate. Sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$) is preferred since it has a dual function of both a source of HOOH and a source of sodium carbonate. Another optional bleaching component is a peracid per se, such as represented by the formula:

$CH_3(CH_2)_w$-NH-C(O)-$(CH_2)_zCO_3H$

wherein z is from 2 to 4 and w is from 4 to 10. The bleaching component can contain, as a bleaching component stabilizer, a chelating agent of polyaminocarboxylic acids, polyaminocarboxylates such as ethylenediaminotetraacetic acid, diethylenetriaminopentaacetic acid, and ethylenediaminodisuccinic acid, and their salts with water-soluble alkali metals. The bleach components, if any, may be added, if any, at a level up to 20%, preferably from about 1% to about 10%, more preferably from about 2% to about 6%.

Nonlimiting examples of additional bleach activators useful herein are to be found in U.S. 4,915,854 to Baker, et al., issued April 10, 1990, U.S. 4,412,934 to Chung and Spadini, issued November 1, 1983 and 4,634,551 to Hardy and Ingram, issued January 6, 1987. The hydrophobic activator nonanoyloxybenzene sulfonate (NOBS) and the hydrophilic tetraacetyl ethylene diamine (TAED) activator are typical, and mixtures thereof can also be used.

Another adjunct ingredient is a photobleach material, particularly the phthalocyanine photobleaches which are described in U.S. Patent 4,033,718 issued July 5, 1977, incorporated herein by reference. Preferred photobleaches are metal phthalocyanine compounds, the metal preferably having a valance of +2 or +3; zinc and aluminum are preferred metals. Such photobleaches are available, for example, as zinc phthalocyanine sulfonate. The photobleach components, if included, are typically in the subject compositions at levels up to about 0.02%, preferably from about 0.001% to about 0.015%, more preferably from about 0.002% to about 0.01%.

Calcium carbonate (also known as Calcarb) is also a well known and often used filler component, especially in a laundry detergent bar. Fillers include minerals, such as talc, bentonite, and hydrated magnesium silicate-containing minerals, where the silicate is mixed with other minerals, e.g., old mother rocks such as dolomite. Sodium sulfate is a well-known filler useful herein. It may be a by-product of the surfactant sulfation and sulfonation processes, or it can be added separately. Filler materials are typically used, if included, at levels up to 40%, preferably from about 5% to about 25%.

Binding agents are especially useful in a laundry detergent bar, for holding it together in a cohesive, yet soluble form. Binding agents include natural and synthetic starches, gums, thickeners, and mixtures thereof. An example of a preferred binding agent is coconut monoethylene amide, and

related materials. Such materials, if included, are typically at levels up to about 3%, preferably about 0.5-2%.

In addition, a hydrotrope, or mixture of hydrotropes, may be present herein. Preferred hydrotropes include the alkali metal, preferably sodium, salts of toluene sulfonate, xylene sulfonate, cumene sulfonate, sulfosuccinate, and mixtures thereof. Preferably, the hydrotrope is added to the linear alkylbenzene sulfonic acid prior to its neutralization. The hydrotrope, if present, will preferably be present at from about 0.5% to about 5% of the laundry detergent bar.

Another useful optional component of the subject composition is an enzyme. The enzyme useful herein has an enzymatic activity, and includes an amylase, a cellulase, a cutinase, a lipase, a peroxidase, a protease, and mixtures thereof. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases. An enzyme is typically incorporated into a laundry detergent composition at levels sufficient to provide a "cleaning-effective amount." The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness-improving effect on substrates such as fabrics, and the like. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. Higher active levels may also be desirable in highly concentrated detergent formulations.

Amylases are particularly suitable for automatic dishwashing purposes. An amylase useful herein includes, for example, -amylases described in GB 1,296,839 to Outtrup H, et al., published November 22, 1972 to Novo Industries A/S of Denmark (hereinafter, "Novo"); RAPIDASE® from International Bio-Synthetics, Inc.; TERMAMYL® from Novo; FUNGAMYL® from Novo; and DURAMYL® from Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, to

Barbesgoard, et al., March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-B-2,075,028 to Barbesgaar, et al., issued March 28, 1984; GB-B-2,095,275 to Murata, et al., issued August 7, 1985 and DE-OS-2,247,832 to Horikoshi and Ikeda, issued June 27 1974. CAREZYME® and CELLUZYME® (Novo) are especially useful. See also WO 91/17243 to Hagen, et al., published November 14, 1991.

Cutinase enzymes suitable for use herein are described in WO 8809367A to Kolattukudy, et al., published December 1, 1988.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034 to Dijk and Berg, published October 30, 1974. See also lipases in Japanese Patent Application 53,20487 to Inugai, published February 24, 1978. This lipase is available from Amano Pharmaceutical Co., Ltd., Nagoya, Japan, under the tradename LIPASE P "AMANO," or "AMANO-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum var. lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., the Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947 to Cornelissen, et al., issued August 31, 1994, also describes a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 to Halkier, et al., published July 7, 1994 A to Novo. See also WO 9205249 to Clausen, et al., published April 2, 1992.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 8909813 A to Damhus, et al., published October 19, 1989.

A suitable example of a protease is a subtilisin, which is obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo. Other examples of a suitable protease includes ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., the Netherlands; as well as Protease A and Protease B as disclosed in EP 130,756 A to Bott, published January 9, 1985. An especially preferred protease, referred to as "Protease D," as described in U.S. Patent 5,679,630 to A. Baeck, et al, issued October 21, 1997, entitled "Protease-Containing Cleaning Compositions," and U.S. Patent 5,677,272 to C. Ghosh, et al, issued October 14, 1997, entitled "Bleaching Compositions Comprising Protease Enzymes."

Glycerine is commonly incorporated in a laundry detergent compositions, especially a liquid detergent composition and a laundry detergent bar composition. If included, it is typically at concentrations up to about 3%, preferably about 0.5-1.5%. Dyes, pigments, germicides, and perfumes can also be added to the bar composition. If included, they are typically at levels up to about 0.5%.

Processing

Laundry detergent processes are known. For example, granular laundry detergent compositions may be manufactured by methods such as blow drying, granulation, and agglomeration. In these processes, it is preferred that exposure of the modified polyethyleneimine polymer and the stilbenedisulfonate brightener to acid are minimized, as extended exposure to acidic conditions may cause these compounds to degrade. Accordingly, in the manufacturing process, it is preferred that the modified polyethyleneimine polymer and the stilbenedisulfonate brightener be added to the laundry detergent composition after the neutralization of the anionic surfactant system (if pre-neutralized anionic surfactants are not used), and homogenized therein.

The laundry detergent bars of the present invention may be processed in conventional soap or detergent bar making equipment with some or all of the following key equipment: blender/mixer, mill or refining plodder, two-stage vacuum plodder, logo printer/cutter, cooling tunnel and wrapper.

In a typical process, a blender mixes the raw materials. Linear alkylbenzene sulfonic acid is added into a mixture of alkaline inorganic salts,

strong electrolyte salts, CFAS, builder, and filler (preferably including sodium carbonate). The resulting partly-neutralized mixture is mechanically worked to effect homogeneity and to complete the neutralization of the mixture. Alternatively, where pre-neutralized LAS paste is available, and economically feasible, it may be used herein. Once the neutralization reaction is completed, the modified polyethyleneimine polymer, and any optional surfactants are added, followed by the stilbenedisulfonate brightener, other DTIs (if present), and any additional adjunct ingredients. The mixing takes from one minute to one hour, with the usual mixing time being from about two to twenty minutes. The blender mix is charged to a surge tank, and conveyed from the surge tank to the mill or refining plodder via a multi-worm conveyer.

After milling or preliminary plodding, the product is then conveyed to a double-vacuum plodder, operating at high vacuum, e.g. 400 to 740 mm of mercury vacuum, so that entrapped air is removed. The product is extruded and cut to the desired bar length, and printed with the product brand name. The printed bar may be cooled, for example in a cooling tunnel, before it is wrapped, cased, and sent to storage.

Typically, in the laundry detergent manufacturing process, the modified polyethyleneimine polymer and the stilbenedisulfonate brightener are added after neutralization of the LAS. However, if pre-neutralized LAS is utilized herein, the modified polyethyleneimine polymer and the stilbenedisulfonate brightener may be added in any order. If desired, polyphosphate can be used as an alkaline salt in the neutralization.

Dye Transfer Inhibition Test

This test determines the Dye Transfer Inhibition capability of test compositions versus a given dye.

A. Material Preparation and Testing Conditions: All steps are conducted at room temperature (about 22-25 °C).

Fabric Preparation

1. Pre-wash a white test fabric in a washing machine five times (5x), using laundry detergent granules which do not contain: perfume, a brightener, and/or a florescent whitening agent. Test fabrics are typically cotton or polycotton fabrics.
2. Cut the test fabric into 5" x 5" swatches, and code the swatch.

Dye Solution Preparation

1. Dissolve in 25 ml deionized water (in a 25 ml volumetric flask) 0.25 g of dye to be tested. Note the λ_{max} of the dye for the colorimeter readings, below.
2. Pipette 10 ml of the dye solution into a 100 ml volumetric flask. Dilute to 100 ml with deionized water.
3. Repeat steps 1 and 2 for each of the dyes to be tested.

B. Test Procedure:

1. Take initial colorimeter (e.g., Ultrascan XE, by Hunter Labs) readings of the swatches. The reading should be taken at the λ_{max} for each specific dye to be tested on that swatch.
2. Using tap water, prepare a 1000 ml wash solution (0.50% by weight, of the laundry detergent composition to be tested) in a 1-liter beaker. Stir the wash solution thoroughly to completely dissolve the laundry detergent.
3. Add 2 ml of the dye solution to the wash solution. Vigorously agitate the wash solution (e.g., with a tergotometer set for 150 rpm) for 2 minutes, to thoroughly disperse the dye into the wash solution.
4. Add the proper coded swatches to their respective wash solutions, and vigorously agitate the wash solution containing the swatch for 5 minutes.
5. Using clean forceps, take out the swatches and immediately place in separate small basins/beakers, with running tap water. Rinse the swatch in running water, with a swirling motion, for exactly 1 minute.
6. Remove each of the swatches, hand squeeze and line dry inside the laboratory.
7. Take final colorimeter readings at λ_{max}, and compare to the control swatches in order to determine the amount of dye transferred onto the test cloths.

C. Technical Paneling:

In addition to the colorimeter tests, a panel of 3 respondents grades the test swatches and the control swatches according to the following scale:

Rating	Descriptor
-4	Control product swatch is definitely much less stained.
-3	Control product swatch is noticeably less stained.
-2	Control product swatch is slightly less stained.
-1	Control product swatch may be less stained.
0	There is no difference between the control and the test product swatches.
1	Test product swatch may be less stained.
2	Test product swatch is slightly less stained.
3	Test product swatch is noticeably less stained.
4	Test product swatch is definitely much less stained.

Examples of the invention are set forth hereinafter by way of illustration and are not intended to be in any way limiting of the invention.

EXAMPLE I

Laundry detergent bars of the present invention, having the following compositions are prepared by conventional blending, milling and plodding procedures.

Component	A	B	C	D
LAS	9.0	7.0	15.0	5.0
Na CFAS	16.0	13.0	5.0	20.0
Na alkyl sulfate (tallow)	5.0	nil	nil	nil
Modified polyethyleneimine polymer	1.0*	0.5**	0.5**	1.0*
Brightener 3	0.50	0.15	0.20	0.15
Brightener 15	nil	0.075	0.10	nil
Brightener 49	0.10	nil	0.05	0.05
Na tripolyphosphate	14.0	18.0	14.0	20.0
PVNO	0.40	nil	nil	0.40
PVP	0.10	nil	0.20	nil
Nonionic Surfactant	nil	nil	nil	2.0
Sodium Carbonate	15.0	5.0	12.0	12.0
Moisture	3.0	3.4	6.0	3.3
Other Adjunct Ingredients	Balance	Balance	Balance	Balance
TOTAL	100	100	100	100

All numbers above represent %, by weight of the final composition

* Modified polyethyleneimine polymer = MW 1200 backbone, and a degree of ethoxylation of 7.

** Modified polyethyleneimine polymer = MW 1800 backbone, and a degree of ethoxylation of 7.

When tested by the Dye Transfer Inhibition Test described herein, for chroma direct yellow, disperse red, and chroma direct scarlet dyes, these laundry detergent bars possessed excellent cleaning and dye transfer inhibition effects for cotton and polycotton fabrics.

EXAMPLE II

The following laundry detergent compositions of the present invention are made according to standard processes. Laundry detergent composition F is in the form of spray dried granules made by a tower process. Laundry detergent composition G is a granular composition made in an agglomerator. Laundry detergent composition H is a liquid detergent composition. Laundry detergent composition I is a paste detergent composition. Laundry detergent composition J is a tablet detergent composition.

Component	F	G	H	I	J
C_{11-13} LAS	5.0	6.0	9.0	15.0	15.0
Na CFAS	20.0	15.0	16.0	5.0	5.0
Na alkyl sulfate (tallow)	nil	5.0	nil	5.0	5.0
Modified polyethyleneimine polymer	2.0*	1.5**	0.5**	1.0*	0.5**
Brightener 3	nil	0.15	0.2	0.15	0.5
Brightener 15	1.0	0.075	0.1	nil	nil
Brightener 49	nil	nil	0.05	0.05	0.1
Na tripolyphosphate	5	nil	nil	nil	15
PVNO	0.5	2.0	1.0	1.0	1.0
PVP	0.5	nil	0.5	nil	nil
Nonionic Surfactant	5.0	2.0	nil	4.0	nil
Sodium Carbonate	4.0	6.0	6.0	6.0	6.0
Moisture	1.0	1.0	50.0	25.0	3.0
Other Adjunct Ingredients	Balance	Balance	Balance	Balance	Balance
TOTAL	100	100	100	100	100

All numbers above represent %, by weight of the final composition

* Modified polyethyleneimine polymer = MW 1200 backbone, and a degree of ethoxylation of 7.

** Modified polyethyleneimine polymer = MW 1800 backbone, and a degree of ethoxylation of 7.

When tested by the Dye Transfer Inhibition Test described herein, for chroma direct yellow, disperse red, and chroma direct scarlet dyes, these laundry detergent bars possessed excellent cleaning and dye transfer inhibition effects for cotton and polycotton fabrics.

WHAT IS CLAIMED IS:

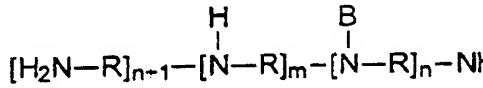
1. A laundry detergent composition comprising, by weight of the final composition:

A. from about 5% to about 30% of an anionic surfactant system, comprising:

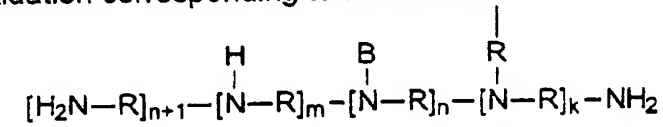
i. a linear alkylbenzene sulfonate; and

ii. a coconut fatty alkyl sulfate;

B. from about 0.05% to about 5% of a modified polyethyleneimine polymer comprising a polyamine backbone prior to modification via quaternization, substitution, or oxidation corresponding to the formula:

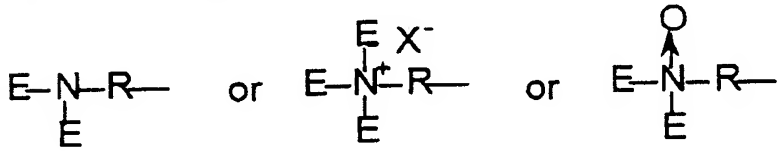


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone prior to modification via quaternization, substitution, or oxidation corresponding to the formula:



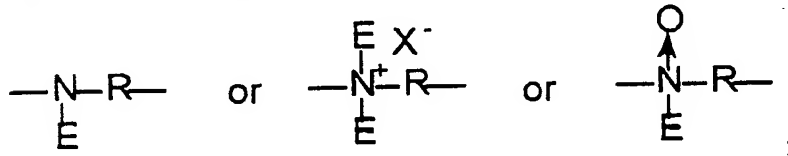
having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

i) V units are terminal units having the formula:



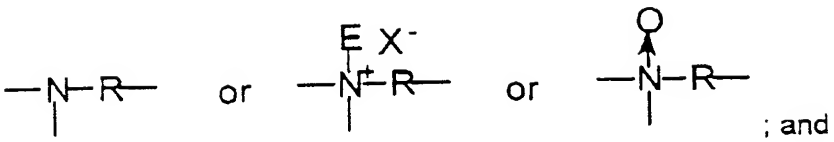
;

ii) W units are backbone units having the formula:



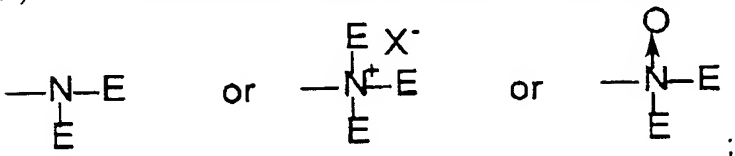
;

iii) Y units are branching units having the formula:



; and

iv) Z units are terminal units having the formula:



;

wherein backbone linking R units are selected from the group consisting of C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R^1 is C_2-C_6 alkylene and mixtures thereof; R^2 is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R^3 is C_1-C_{18} alkyl, C_7-C_{12} arylalkyl, C_7-C_{12} alkyl substituted aryl, C_6-C_{12} aryl, and mixtures thereof; R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, and mixtures thereof; R^5 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, -C(O)-, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof; R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene; E units are selected from the group consisting of hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is hydrogen, C_1-C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures

thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1;

C. from about 0.01% to about 5% of a stilbenedisulfonate brightener; and

D. the balance adjunct ingredients.

2. A laundry detergent bar composition comprising the laundry detergent composition of Claim 1.

3. The laundry detergent composition of Claim 1, wherein the ratio of linear alkylbenzene sulfonate to coconut fatty alkyl sulfate is from about 19:1 to 1:9, by weight, in the final composition.

4. The laundry detergent composition of Claim 1, wherein the final composition is substantially free of soap.

5. The laundry detergent composition of Claim 1, wherein the anionic surfactant system further comprises a tallow alkyl sulfate.

6. A laundry detergent composition according to Claim 1, wherein the adjunct ingredient comprises a builder selected from the group consisting of phosphates, pyrophosphates, orthophosphates, tripolyphosphates, higher polyphosphates, and mixtures thereof.

7. A laundry detergent composition according to Claim 1, wherein the adjunct ingredient comprises an other dye transfer inhibitor.

8. A laundry detergent composition according to Claim 1, wherein the adjunct ingredient comprises a bleach.

9. A laundry detergent composition according to Claim 1, wherein the adjunct ingredient comprises an enzyme.

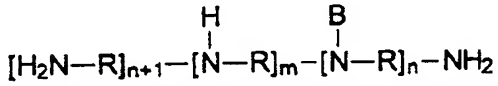
10. A laundry detergent bar composition comprising, by weight of the final composition:

A. from about 5% to about 30% of an anionic surfactant system, comprising:

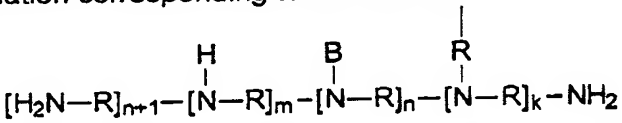
i. a linear alkylbenzene sulfonate; and

ii. a coconut fatty alkyl sulfate;

B. from about 0.05% to about 5% of a modified polyethyleneimine polymer comprising a polyamine backbone prior to modification via quaternization, substitution, or oxidation corresponding to the formula:

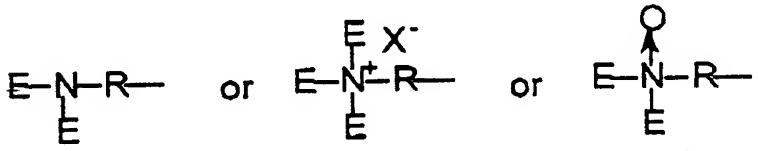


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone prior to modification via quaternization, substitution, or oxidation corresponding to the formula:

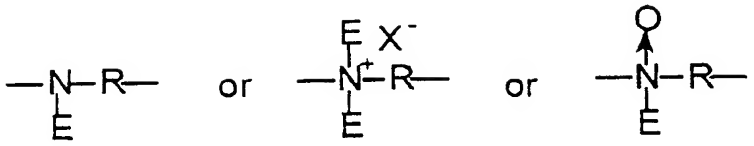


having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

i) V units are terminal units having the formula:

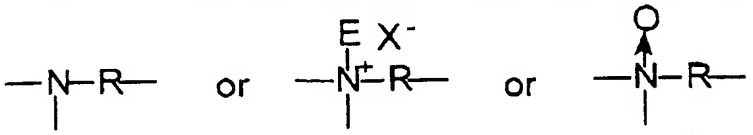


ii) W units are backbone units having the formula:



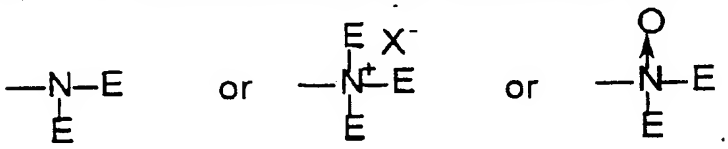
;

iii) Y units are branching units having the formula:



; and

iv) Z units are terminal units having the formula:



;

wherein backbone linking R units are selected from the group consisting of C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)_z(R^1O)_yR^1(OCH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R^1 is C_2-C_6 alkylene and mixtures thereof; R^2 is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R^3 is C_1-C_{18} alkyl, C_7-C_{12} arylalkyl, C_7-C_{12} alkyl substituted aryl, C_6-C_{12} aryl, and mixtures thereof; R^4 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, C_8-C_{12} arylalkylene, C_6-C_{10} arylene, and mixtures thereof; R^5 is C_1-C_{12} alkylene, C_3-C_{12} hydroxyalkylene, C_4-C_{12} dihydroxy-alkylene, C_8-C_{12} dialkylarylene, -C(O)-, $-C(O)NHR^6NHC(O)-$, $-R^1(OR^1)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1OCH_2CH(OH)CH_2-$, and mixtures thereof; R^6 is C_2-C_{12} alkylene or C_6-C_{12} arylene; E units are selected from the group consisting of hydrogen, C_1-C_{22} alkyl, C_3-C_{22} alkenyl, C_7-C_{22} arylalkyl, C_2-C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof;

provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is hydrogen, C_1-C_6 alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1;

C. from about 0.01% to about 5% of a stilbenedisulfonate brightener; and

D. the balance adjunct ingredients,

wherein the final composition is substantially free of soap, wherein the ratio of linear alkylbenzene sulfonate to coconut fatty alkyl sulfate is from about 19:1 to 1:9, by weight, in the final composition, and wherein the final composition is in the form of a bar.

INTERNATIONAL SEARCH REPORT

In. .ational Application No
PCT/US 98/15349

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/00 C11D1/37 C11D3/37 C11D3/42 //C11D1:22, C11D1:14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 42283 A (THE PROCTER & GAMBLE CO.) 13 November 1997 see page 4, line 5 - page 5, line 37 see page 7, line 5 - page 19, line 10 see page 24, line 19 - line 26	1-3,5-9
A	see claims	4,10

E	WO 98 53040 A (THE PROCTER & GAMBLE CO.) 26 November 1998 see page 4, line 9 - page 5, line 24 see page 9, line 7 - page 13, line 14 see page 14, line 5 - line 18	1-10

Y	WO 95 27038 A (THE PROCTER & GAMBLE CO.) 12 October 1995 see claims; examples	1-10

	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 March 1999	29/03/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Serbetsoglou, A

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

In. .ational Application No
PCT/US 98/15349

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate. of the relevant passages	Relevant to claim No.
Y	WO 95 32272 A (THE PROCTER & GAMBLE CO.) 30 November 1995 cited in the application see claims; example VIII	1-10

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

In. ational Application No
PCT/US 98/15349

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9742283 A	13-11-1997	NONE	
WO 9853040 A	26-11-1998	AU 3142697 A	11-12-1998
WO 9527038 A	12-10-1995	CN 1145093 A	12-03-1997
		CN 1145094 A	12-03-1997
		CN 1145095 A	12-03-1997
		WO 9527036 A	12-10-1995
		WO 9527037 A	12-10-1995
WO 9532272 A	30-11-1995	AU 2387095 A	18-12-1995
		BR 9507691 A	23-09-1997
		CA 2189749 A	30-11-1995
		EP 0760846 A	12-03-1997
		JP 10500717 T	20-01-1998
		US 5565145 A	15-10-1996